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Infrared spectra of benzoic acid monomers and dimers in argon matrix

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Abstract

The infrared spectra of benzoic and deuterobenzoic acids isolated in Ar matrices were measured using the matrix-to-sample (M/S) ratios 750 and 250. The spectra were interpreted both by AM1 semiempirical and variational methods. The calculation of the potential energy surface of benzoic acid monomer shows that only the *syn* conformer of benzoic acid must be present in the matrix, which is in complete agreement with experimental data obtained previously. Matrix annealing mainly favours the formation of cyclic symmetrical dimers with two intermolecular H-bonds. The frequency shifts of some vibrations of the COOH group on association are measured. More complex aggregates were revealed in the matrix isolation measurements.

Keywords: Infrared spectrometry, low-temperature; Matrix isolation; Benzoic acid; Autoassociation; Quantum-chemical calculations; Normal coordinate analysis

1. Introduction

Recently, low-temperature matrix infrared (IR) spectroscopy was applied to study the molecular structure of some amino acids belonging to the aliphatic series [1–3]. The molecules of amino acids are conformationally labile due to internal rotation. Conformational changes and association produce similar effects in the IR spectra of amino acids isolated in inert gas matrices. It is therefore important to derive information which might permit reliable separation of the association and conformation effects. Such information can be obtained from IR spectroscopy of self-association of conformationally restricted compounds by changing the trapped molecules in the matrix. Benzoic acid was chosen as the object of present study, because it is the simplest aromatic acid to be used as a suitable model to study molecular structures and spectral features of carboxyl compounds and their complexes.

The monomers of benzoic acid were preliminary studied [4] and it was found that the molecule has one conformer. A small amount of H-bonded self-associates were also detected in the matrices. It is therefore clear that upon increasing the molecule concentration the bands of the self-associates appreciably gain intensity. By this means a more complete set of vibrational frequencies of self-associates can be obtained. The analysis of these frequencies would

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then specify the self-association effect on the IR spectra and suggest the structures of the possible aggregates.

Thus, the goal of this work is to interpret the IR spectra and to identify the structure of the matrix-isolated benzoic acid monomer and its self-associates. A further aim is to find out the regularities of the spectral features brought about by self-association of carboxyl containing compounds isolated in inert matrices.

For this reason, the IR spectra of benzoic acid isolated in Ar matrix were obtained for samples with $M/S = 750$ and 250. For making the spectral analysis more reliable similar spectra were obtained for deuterobenzoic acid. The structures and the relative energies were calculated by the AM1 semiempirical method and the vibrational frequencies of the most stable monomer and dimer were calculated by the variational and AM1 methods.

2. Experimental

The updated Specord IR 75 grating spectrometer (Carl Zeiss, Jena) was used to measure the IR spectra. The cryostat used for matrix IR spectroscopy is described elsewhere [5]. To exclude the influence of atmospheric H_2O and CO_2 vapour, the spectrometer was sealed and blown through with dry nitrogen during the experiment. The samples were prepared by simultaneous deposition of the substance and the matrix gas onto a cooled optic CsI substrate. The matrix gas was 99.99% Ar. The optic substrate temperature was maintained at 17 K during matrix deposition to obtain a sample with optimal scattering. When the spectra were recorded, the temperature was lowered to 12 K to prevent matrix overheating in the spectrometer beam.

The samples with $M/S = 750$ and 250 for benzoic acid and with $M/S = 750$ for deuterobenzoic acid were prepared. The matrix-to-sample ratio was specified with a quartz microbalance. Deuterobenzoic acid was prepared by double recrystallization of benzoic acid from D_2O solution. The compounds were evaporated from a Knudsen cell at 46°C.

Two samples (benzoic acid, $M/S = 250$; deuterobenzoic acid, $M/S = 750$) were annealed at 30 K for 30 min. To retain the surface Ar layer from evaporation and to keep the matrix homogeneous in composition, the samples were covered by protective films before annealing. A heavier-than-matrix gas (Kr) was deposited over the sample at $T = 17$ K for 15 min.

3. Calculations

The structural and energy parameters of the benzoic acid monomers and dimers were calculated by the AM1 semiempirical method [6]. The molecular geometries were fully optimized with the MOPAC6 program package [7] using the "PRECISE" option (gradient norm less than 0.01). To find parameters of possible minima and transition states, the potential energy surface of benzoic acid monomer was calculated. To do this, the heat of formation was calculated as a function of the dihedral angles C–C–C–O and O=C–O–H. At each step the angles were changed by 10°. In addition, the torsion potentials of the rotation around C–COOH and C–O bonds were calculated.

The experimental IR spectra were interpreted using the variational method. The force constants of the molecule studied were transferred from force fields of related compounds. Their variation provided a set of calculated frequencies mostly approaching the experimental results. A special program package [8] was used for normal coordinate analysis.

The benzoic acid monomer has a planar structure and belongs to the C_s point group. It has 39 normal vibrations, namely 27 A' (planar) + 12 A'' (out-of-plane) and these vibrations are IR active. The cyclic benzoic acid dimer also has a planar structure and belongs to the C_{2h} point group. The total number of normal vibrations is 84 including 29 A_g (planar) + 28 B_u (planar) + 14 A_u (out-of-plane) + 13 B_g (out-of-plane). The B_u and A_u vibrations are IR active, while the A_g and B_g ones are Raman active.

Variations of the bond lengths, bond angles and dihedral angles of the ring and attached atoms were used as internal coordinates of benzoic acid monomer. These and the additional six coordinates were used for the cyclic dimer. The additional coordinates describe the motions of two molecules of the dimer relative to each other, these are the O · · · H symmetrical stretching (A_g), the O · · · H antisym-

metrical stretching (B_u), the O · · · H–O symmetrical bending (A_g), the O · · · H out-of-plane bending symmetrical (B_g), the O · · · H out-of-plane bending antisymmetrical (A_u) and the O · · · H out-of-plane twisting (A_u).

The interpretation of spectra of large systems (e.g., benzoic acid dimer) by the variational method is very complicated. The AM1 method (MOPAC6) was therefore used as a supplementary one. First, the vibrational frequencies of the benzoic acid monomer were calculated ("PRECISE" and "FORCE" options). In the analysis of experimental and theoretical (AM1) frequencies, scaling factors were calculated for each type of vibrations. The frequencies of the cyclic dimer were then calculated and changed by using the corresponding scaling factors obtained for the monomer. These refined frequencies were used to interpret the experimental spectra.

4. Results and discussion

The IR spectroscopic studies of the dimerization processes and investigation of the molecular structure of benzoic acid aggregates isolated in Ar matrices should reasonably start from the analysis of the monomeric molecules. The first step was therefore to carry out the experimental and theoretical investigation of the benzoic acid monomers. Early we found that conformational and associate effects are very similar in the IR spectra of carboxyl containing compounds isolated in matrices [4]. Special interest was therefore focused on the conformational analysis of the benzoic acid molecules.

4.1. IR spectra and structure of the monomer

To determine the structure and the relative energies of possible conformers, the potential energy surface of benzoic acid was calculated by the AM1 method. Point-by-point optimization was carried out for the torsion angles O=C–O–H and C–C–C–O (Fig. 1) with a 10° step in the ranges 0–180° and 0–90°, respectively. The potential energy of benzoic acid as a function of the torsion angles is shown in Fig. 2. For clarity, the entire surface of both torsion angles within 0–360° is depicted. The torsion poten-

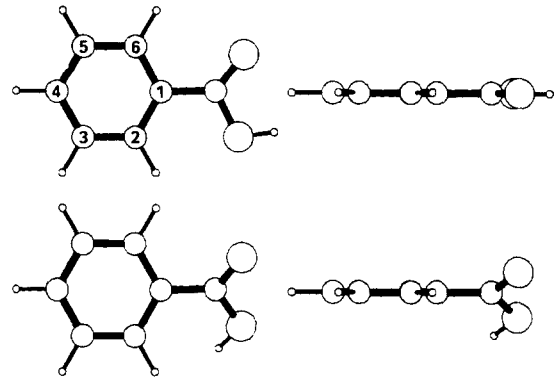

Fig. 1. Calculated structures of *syn* (upper) and *anti* (lower) benzoic acid conformers.

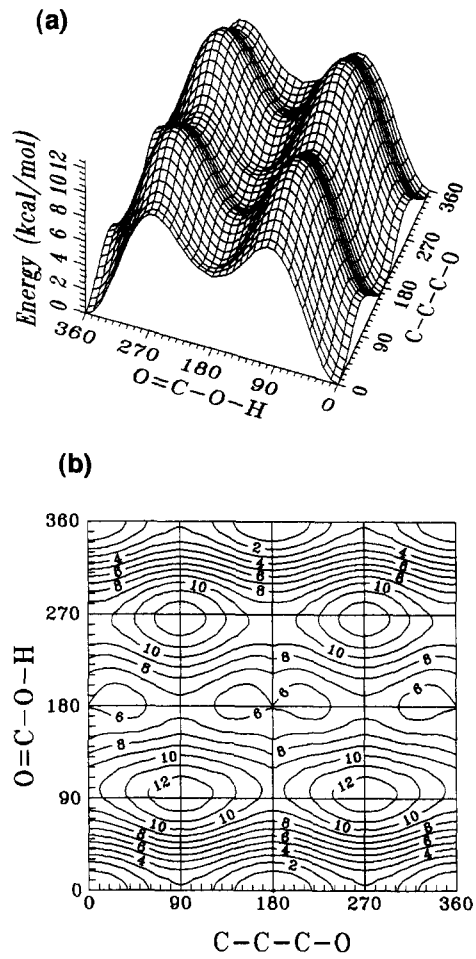

Fig. 2. Potentional energy surface of benzoic acid: (a) three-dimensional plot, (b) two-dimensional plot.

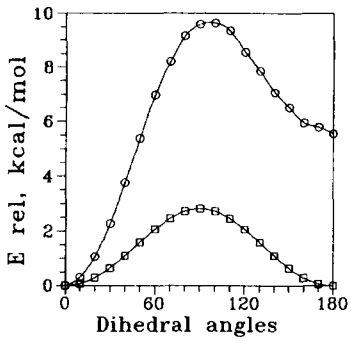

Fig. 3. Calculated torsional potentials in benzoic acid for the internal rotation of (○) the hydroxyl group and (□) the carboxyl group.

tials referring to the rotation about the C–C and C–O bonds are shown in Fig. 3.

Two minima of the potential energy were found and they correspond to the two conformers. The global minimum refers to the *syn* conformer (Fig. 1a) having a planar structure ($\theta_{O=C-O-H} = 0°$ and $\theta_{C-C-C-O} = 0°$). The local minimum ($\theta_{O=C-O-H} = 180°$and $\theta_{C-C-C-O} = 33.3°$) refers to the *anti* conformer (Fig. 1b) with the relative energy of 5.5 kcal mol^{-1}. The barrier of the *syn* → *anti* transition is 9.6 kcal mol^{-1} (Fig. 3).

The most important parameters of the benzoic acid conformers corresponding to the potential energy minima and transition states are presented in Table 1. For comparison, results of non-empirical calculations at the MP2/6-311 + + G**//MP2/6-31G* level of theory [9] are given. It is seen that the AM1 calculation slightly underestimates the relative energies of the transition states, however, the general agreement with ab initio results is still good. The relative energy of the *syn* and *anti* conformers and the barrier between them suggest that isolated benzoic acid exists as *syn* conformer. This was taken into account while interpreting the IR spectra of benzoic acid and its deutero-analogue. The observed frequencies and relative peak intensities are given in Table 2.

The IR spectra were interpreted using the variational method. The force constants of benzoic acid were transferred from the force field of closely related molecules (benzene, acetic acid). The force constants were then refined to achieve a set of calculated frequencies, which most closely approached the experimental frequencies. This procedure (solution of inverse problem) was performed simultaneously for benzoic acid and its deutero-analogue, i.e. the same force constants were used to calculate two spectra at once. This ensures higher reliability of the force constants. The calculated frequencies of normal vibrations and the potential energy distributions are presented in Table 2.

Since all details are given quite thoroughly, let us confine our consideration to the most important vibrations of benzoic acid in the Ar matrix.

The OH stretching band at 3567 cm^{-1} and OD stretching band at 2631 cm^{-1} have distinct singlet structures. This indicates that only one conformer is present in the matrix and supports the results of AM1 calculation of relative stability of conformers. On the other hand, this rules out the conformational splitting as a reason of band splitting in the IR spectra of benzoic acid. The isotopic shift $\omega_{OHstr}/\omega_{ODstr}$ is 1.356 and it is consistent with the results of acetic acid (1.356 [10]), glycine (1.354 [3]) and proline (1.355 [2]).

In the C=O stretching region (1760–1700 cm^{-1}), the IR spectra of benzoic and deuterobenzoic acid have several merged bands. We believe that the closely spaced bands at 1752, 1751, 1743 cm^{-1} observed in the spectrum of benzoic acid and at

Table 1
Some characteristics of the benzoic acid conformers

	AM1	MP2/6-311 + + G**//MP2/6-31G* [9]
Relative energy (kcal mol^{-1})		
syn (M) [a]	0.	0.
anti (M) [a]	5.5	6.34
anti planar [b] (TS) [a]	5.9	7.21
syn perpendicular [c] (TS) [a]	2.8	5.04
perpendicular [d] (TS) [a]	9.6	12.57
$\theta_{C-C-C-O}$ for *anti* (°)	33.3	22.9 [e], 30.6 [f]
Dipole moment (Debye)		
syn	2.41	
anti	4.93	

[a] M and TS refer to energy minimum and transition state, respectively.
[b] $\theta_{O=C-O-H} = 180°$ and $\theta_{C-C-C-O} = 0°$.
[c] $\theta_{O=C-O-H} = 0°$ and $\theta_{C-C-C-O} = 90°$.
[d] $\theta_{O=C-O-H} = 90°$ and $\theta_{C-C-C-O} = 0°$.
[e] At the HF/6-31G* level [9].
[f] At the MP2/6-31G* level [9].

1747, 1745, 1741 cm^{-1} in the spectrum of deuterobenzoic acid are due to site splitting, i.e. different types of molecule packing in the Ar matrix. The matrix splitting up to 10 cm^{-1} is typical for the IR spectra of molecules isolated in Ar. The very weak bands 1699 cm^{-1} (benzoic acid) and 1697 cm^{-1} (deuterobenzoic acid) are likely to refer to vibrations of associated molecules. The proof comes from studies of concentration dependence of the spectra and will be considered below. The correlation between the number of monomers, dimers and larger associates in the matrix and the total concentration of substance was studied recently [11]. Using this correlation it is easy to estimate that in the sample with $M/S = 750$ about 85% of the molecules of benzoic acid exist as monomers and 15% form associates. The structure of associates is defined during matrix deposition and only a small part of molecules form H-bonded associates.

In our study the interpretation of the spectra by the variational method was supplemented with quantum-chemical calculations of the vibrational frequencies using the AM1 method. The comparison of the experimental and calculated (AM1) frequencies allows us to estimate scaling factors of each vibration (Table 3). The AM1 results are in agreement with the experimental spectra. For most frequencies the error is not more than 10%, although the potential energy distributions (PEDs) based on the AM1 and variational methods diverge considerably for few low-lying vibrations. For vibrations above 400 cm^{-1} the averaged scaling factor is 0.9604 for benzoic acid and 0.9614 for deuterobenzoic acid. However, the average values of scaling factors calculated separately for planar and out-of-plane vibrations are much different, that is 0.9342 and 1.0259 (benzoic acid) and 0.9349 and 1.0277 (deuterobenzoic acid). The scaling factors obtained for the monomer were used in the analysis of the IR spectra of benzoic acid associates.

4.2. Calculated structure of benzoic acid dimers

Our next step was to investigate the structure of benzoic acid associates. The geometries and heats of formation of benzoic acid dimers were calculated by the AM1 method. The initial structures of dimers were selected assuming that the intermolecular H-bonds C=O · · · H–O are formed at self-association. First, a symmetrical cyclic dimer with two H-bonds was calculated. Then calculations were performed for a series of open (linear) dimers with one H-bond. The cyclic dimer was found to be the most stable associate. The H-bond energies of cyclic and linear dimers are 6.3 and 4.2 kcal mol^{-1}, respectively. The comparison of the heats of formation of cyclic dimer calculated by AM1 and ab initio methods shows that the AM1 method tends to underestimate considerably the intermolecular interaction energy. According to ab initio calculations, the heat of formation of the cyclic dimer is -16.5 kcal mol^{-1} (STO 3G) and -21.2 kcal mol^{-1} (4-31G) [12].

4.3. IR spectra of matrix-isolated benzoic acid dimers

Two experimental methods used to obtain the vibrational frequencies of benzoic acid associates were the comparison of the IR spectra obtained for samples with different concentrations of benzoic acid and the comparison of the IR spectra obtained before and after matrix annealing. The spectra of benzoic acid with $M/S = 750$ and 250 and the spectrum of deuterobenzoic acid with $M/S = 750$ were measured. The two samples (benzoic acid, $M/S = 250$ and deuterobenzoic acid, $M/S = 750$) were annealed and their spectra were measured again. Using the recently developed technique of quantitative assessment of monomers, dimers and larger associates in matrices [11], we estimated that the abundance of dimers in our samples was 15% ($M/S = 750$) and 50% ($M/S = 250$). At matrix annealing, the structure of the associates is ordered due to orientational diffusion of the molecules. This usually reduces the half-width and increases the intensities of the bands in the IR spectra.

The spectra of samples with different M/S, as well as the spectra of the annealed samples, are shown in Figs. 4–6. The observed and calculated frequencies of the cyclic dimer which were found to differ from frequencies of monomeric benzoic acid are listed in Table 4. The analysis of the spectra allows us to draw the following conclusions:

(i) The associates of benzoic acid have a strictly ordered structure. This is evident from the vibrational bands whose half-width slightly exceed those of monomers. It is known that even in the solid state

Table 2
Observed and calculated frequencies of benzoic acid and deuterobenzoic acid (Ar matrix, 12 K) [a]

Benzoic acid					Deuterobenzoic acid			
ω_{obs}	I	ω_{calc}	Assignment [b,c]	No [d]	ω_{obs}	I	ω_{calc}	Assignment [b,c]
3567	0.43	3571	OH str [100]		2631	0.42	2633	OD str [99]
					2620	sh		
3098	0.02	3096	C4H str [96]	13	3099	0.02	3096	C4H str [96]
3079	0.03	3075	C3H str [49], C5H str [49]	20b	3081	0.02	3075	C3H str [49], C5H str [49]
3068	0.03	3067	C3H str [48], C5H str [48]	20a	3066	0.03	3067	C3H str [48], C5H str [48]
3041	0.02	3041	C2H str [49], C6H str [49]	7a	3039	0.01	3041	C2H str [49], C6H str [49]
3012	0.01	3012	C2H str [49], C6H str [49]	7b	3013	0.01	3012	C2H str [49], C6H str [49]
1755	sh				1754	sh		
1752	1.50	1758	C=O str [68]		1747	sh		
1751	1.49				1745	1.52	1754	C=O str [68]
1743	0.10				1741	sh		
1738	0.09				1717	0.06		
1699	0.09		dimer C=O str		1697	0.08		dimer C=O str
1606	0.22	1607	ring str [71]	8b	1605	0.24	1607	ring str [71]
1590	0.04	1595	ring str [77]	8a	1591	0.02	1595	ring str [77]
					1587	0.03		
					1566	0.02		
1496	0.03	1500	ring str [35], C3H bend [18], C5H bend [16]	19a	1495	0.06	1499	ring str [35], C3H bend [18], C5H bend [16]
1493	0.03				1490	0.02		
1456	0.26	1457	C4H bend [35], ring str [27]	19b	1455	0.25	1457	C4H bend [35], ring str [28]
1430	0.07		dimer		1443	0.04		dimer
1383	0.11	1372	CH bend [25], C–COOH str [20]					
1380	0.13				1380	0.02 [h]		
					1365	0.04	1360	CH bend [32], C–COOH str [20], C–O str [17]
1347	1.00	1325	CH bend [59], ring str [23]	14	1346	0.10 [h]		
1322	0.04		dimer		1335	0.03		
1316	0.08		dimer		1320	0.77	1320	CH bend [49], ring str [21], C–O str [11]
					1317	0.58		
1297	0.04		dimer		1303	1.08	1277	ring str [88]
					1294	0.44		
1278	sh [e]							
1275	0.20	1276	ring str [88]	3				
1271	0.15							
1255	sh [f]							
1251	0.07				1249	0.04		
1248	sh							
1228	0.03				1206	0.02		
1185	0.54	1183	CH bend [67], OH bend [19]	2	1185	0.06 [h]		
					1179	0.07	1181	CH bend [96]
1169	1.09	1179	OH bend [47], CH bend [31]		1169	0.15 [h]		
					1166	sh		
1164	0.05							
1159	0.04							
1149	0.07							

Table 2 (continued)

Benzoic acid					Deuterobenzoic acid			
ω_{obs}	I	ω_{calc}	Assignment [b,c]	No [d]	ω_{obs}	I	ω_{calc}	Assignment [b,c]
1135	0.05 [g]							
1110	0.06	1129	CH bend [79], ring str [15]	9b	1109	0.08	1132	CH bend [57], ring str [15]
1100	0.09				1101	0.04		
					1090	0.25	1124	CH bend [49], ring str [19], ring bend [12]
1086	0.68	1114	C–O str [29], ring bend [15], OH bend [13]		1086	0.07 [h]		
					1068	0.13	1055	ring str [63], CH bend [24]
1066	0.80	1055	ring str [63], CH bend [24]	18b	1066	sh [h]		
1063	sh	1049	CH oop [74], ring oop [22]	5	1051	0.01	1049	CH oop [74], ring oop [22]
1027	0.29	1037	ring str [43], ring bend [35]	18a	1026	0.18	1037	ring str [43], ring bend [35]
		991	ring str [87]	12	995	0.03	991	ring [85]
					985	0.71		
					984	0.75	967	OD bend [64]
		977	CH oop [94]	17a			977	CH oop [94]
937	0.03	936	CH oop [78]	17b	937	0.03	936	CH oop [78]
		855	CH oop [54], ring oop [35]	10a	846	0.02	854	CH oop [53], ring oop [35]
		835	CH oop [100]	10b	843	0.02	835	CH oop [100]
767	0.09	750	ring str [30], C–COOH str [20]	1	734	0.08	734	ring str [42], C–COOH str [18]
759	0.06							
713	sh							
711	2.27	724	CH oop [92]	4	711	sh [h]		
					708	1.87	724	CH oop [92]
687	0.08	667	ring bend [37], C=O bend [37]	6b	685	0.09	660	ring bend [66], CH bend [18]
		653	ring bend [49], C–O bend [27]				604	O–C=O bend [44], OD bend [27]
628	0.97	636	OH oop [96]		628	0.08 [h]		
					591	sh	576	CH oop [49], C=O oop [22], ring oop [22]
					584	1.41		
568	0.53	576	CH oop [39], C=O oop [22], ring oop [22]	11	568	0.05 [h]		
					565	0.05		
565	0.69	545	C–O bend [37], C=O bend [25]				540	C–O bend [42], C=O bend [22]
491	0.02	506	ring oop [80], CH oop [17]	6a	488	0.05	508	ring oop [44], OD oop [33]
					461	0.15	503	OD oop [42], ring oop [34]
421	0.13	444	C = O oop [59], ring oop [30]				419	OD oop [40], C=O oop [35]
		348	ring bend [30], O–C=O bend [27]	15			345	ring bend [29], O–C=O bend [27]
		168	C–COOH bend [78]				166	C–COOD bend [78]
		160	C–COOH oop [66]				157	C–COOD oop [65]
		132	C–COOH tors [96]				131	C–COOD tors [96]

[a] Matrix ratio 1:750.
[b] str, stretching; bend, bending; oop, out-of-plane.
[c] Potential energy distributions (%) are given in square brackets.
[d] Phenyl vibrations are described in terms of approximate Wilson mode.
[e] Overtone 711 + 568 = 1279 cm^{-1}.
[f] Overtone 2 × 628 = 1256 cm^{-1}.
[g] Overtone 2 × 568 = 1136 cm^{-1}.
[h] Non-deuterated benzoic acid.

benzoic acid exists as H-bonded cyclic dimers [13]. We may thus assume that similar dimers are formed in a low-temperature matrix.

(ii) Comparison of the spectra shows a small number of new bands assigned to the vibrations of the COOH group of associates.

Let us consider in detail some spectral regions where vibrations of associates are more pronounced. The region of the OH (OD) stretching vibrations is shown in Fig. 4. The IR spectrum obtained immediately after deposition (deuterobenzoic acid, $M/S =$ 750) contains no bands of associates (Fig. 4b). After

Table 3
Scaling factors for benzoic acid and deuterobenzoic acid calculated as $\omega_{obs}/\omega_{AM1}$ [a]

Benzoic acid				Deuterobenzoic acid			
ω_{obs}	ω_{AM1}	S.f. [c]	Assignment	ω_{obs}	ω_{AM1}	S.f. [c]	Assignment
3567	3427	1.0408	OH str	2631	2500	1.0524	OD str
3098	3182	0.9736	CH str	3099	3182	0.9739	CH str
3079	3199	0.9625	CH str	3081	3199	0.9631	CH str
3068	3191	0.9614	CH str	3066	3191	0.9608	CH str
3041	3172	0.9587	CH str	3039	3172	0.9581	CH str
3012	3170	0.9501	CH str	3013	3170	0.9504	CH str
1752	2077	0.8435	C=O str	1745	2068	0.8438	C=O str
1606	1776	0.9043	ring str	1605	1776	0.9037	ring str
1590	1765	0.9008	ring str	1591	1746	0.9019	ring str
1496	1638	0.9133	ring str	1495	1636	0.9138	ring str
1456	1573	0.9256	C4H bend	1455	1573	0.9250	C4H bend
1383	1541	0.8975	CH bend	1365	1522	0.8968	CH bend
1347	1380	0.9761	CH bend	1320	1381	0.9558	CH bend
1275	1358	0.9389	ring str	1303	1358	0.9595	ring str
1185	1315	0.9011	CH bend	1179	1315	0.8966	CH bend
1169	1435	0.8146	OH bend	984	1137	0.8654	OD bend
1110	1229	0.9032	CH bend	1109	1229	0.9024	CH bend
1086	1198	0.9065	C–O str	1090	1198	0.9098	CH bend
1066	1185	0.8996	ring str	1068	1177	0.9074	ring str
1049 [b]	1013	1.0355	CH oop	1051	1013	1.0375	CH oop
1027	1168	0.8793	ring str	1026	1169	0.8777	ring str
991 [b]	1089	0.9100	ring str	995	1073	0.9273	ring str
977 [b]	995	0.9819	CH oop	977 [b]	995	0.9819	CH oop
937	972	0.9640	CH oop	937	972	0.9640	CH oop
855 [b]	894	0.9564	CH oop	846	894	0.9463	CH oop
835 [b]	825	1.0121	CH oop	843	825	1.0218	CH oop
767	886	0.8656	ring bend	734	863	0.8505	ring bend
711	723	0.9834	CH oop	708	723	0.9792	CH oop
687	657	1.0457	ring bend	685	657	1.0426	ring bend
653 [b]	646	1.0108	ring bend	604 [b]	624	0.9679	O–C=O bend
628	536	1.1716	OH oop	461	373	1.2359	OD oop
568	609	0.9327	CH oop	584	607	0.9621	CH oop
565	509	1.0707	C–O bend	540 [b]	507	1.0651	C–O bend
491	411	1.1946	ring oop	488	439	1.1116	ring oop
421	410	1.0268	C=O oop	419 [b]	404	1.0371	OD oop
348 [b]	371		ring bend	345 [b]	371		ring bend
168 [b]	199		C–COOH bend	166 [b]	196		C–COOD bend
160 [b]	149		C–COOH oop	157 [b]	147		C–COOD oop
132 [b]	43		C–COOH tors	131 [b]	42		C–COOD tors

[a] The spectra are not measured in the region lower than 400 cm^{-1} and scaling factors for AM1 frequencies in this region are not calculated.
[b] Frequency is absent in the experimental spectrum and calculated by the variational method.
[c] S.f., scaling factor.

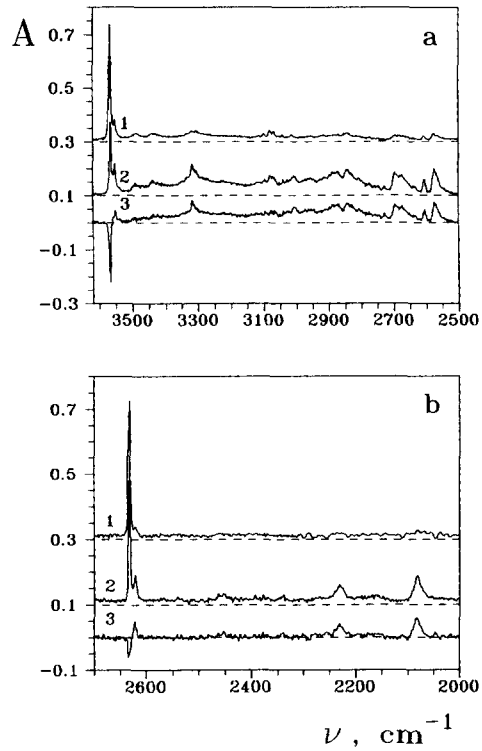

Fig. 4. O–H (O–D) stretching region. (a) Benzoic acid (M/S = 250). (b) Deuterobenzoic acid (M/S = 750). (1) Spectra after deposition at 17 K. (2) Spectra after matrix annealing at 30 K for 30 min. (3) Difference spectra (3 = 2 − 1).

annealing two new bands appear at 2230 and 2081 cm^{-1}. The more intense band was assigned to the asymmetric OD stretching vibration of the cyclic dimer. The shift against the monomer band (2631 cm^{-1}) is 550 cm^{-1}. The weaker 2230 cm^{-1} band likely corresponds to the linear dimer. The low-frequency shoulder of the 2631 cm^{-1} band (OD stretching vibration of monomer) observed after annealing of the matrix may be due to the formation of the linear dimer with single H-bond. This shoulder may be assigned to the stretching vibration of unbound OD group in the linear dimer. This assumption is, however, still open to discussion. The intensity redistribution of the merged bands is frequent in the matrix IR spectra. It is usually caused by site splitting.

Let us now proceed to the spectra obtained for the benzoic acid sample with $M/S = 250$ (Fig. 4a). Immediately after deposition of the sample, the spectrum has a set of broad bands produced by associates. These are observed in a wide range (3500–2500 cm^{-1}) and can be assigned to the disordered associates which were fixed in the matrix during deposition. This result is quite natural because there are only 50% isolated monomers of benzoic acid in the sample with $M/S = 250$. On annealing, the bands become more intense and the basic line runs higher.

Table 4
Observed and calculated frequencies of the benzoic acid cyclic dimer (Ar matrix, 12 K) [a]

ω_{obs}		I_{obs} [b] for M/S			ω_{calc} by		Assignment
Monomer	Dimer	750	250	250 annealed	AM1 scaled	Variational method	
3567	3312	–	0.02	0.05			OH str
	2605	–	0.02	0.04			OH str
	2575	–	0.03	0.08	3370	2592	OH str
1752	1738	0.09	0.18	0.44			C=O str
	1699	0.09	0.26	1.12	1720	1703	C=O str
1169	1430	0.07	0.03	0.16	1269	1421	OH bend
1380	1322	0.04	0.06	0.28	1355	1328	C–O str
	1316	0.08	0.06				
1185	1297	0.04	0.07	0.40	1237	1289	CH bend, OH bend
	1228	0.03	0.03	0.07			
628	960	–	0.02	0.07	727	952	OH oop
568	670	–	–	0.09	613	665	C=O bend
	640	–	–	0.03			
421	547	–	–	0.03	465	541	C=O oop

[a] str, stretching; bend, bending; oop, out-of-plane.
[b] Related peak intensities.

We believe these features are the evidence for the formation of associates larger than dimers. This makes the assignment of all bands in this region quite difficult. The calculation suggests that only the lowest-lying in this region band at 2575 cm^{-1} may be assigned to the asymmetric stretching vibration of the bound OH group of the cyclic dimer (Table 4).

In Fig. 5 the C=O stretching region is presented. No bands of vibrations of associates were observed immediately after deposition in the IR spectrum of deuterobenzoic acid sample with $M/S = 750$ (see Fig. 5b). After annealing, a new band at 1697 cm^{-1} appears and this band was assigned to the vibration of the cyclic dimer (Table 4). For the benzoic acid sample with $M/S = 250$ a similar band (1699 cm^{-1}) is observed in the spectrum taken immediately after deposition (Fig. 5a). After annealing, the peak intensity of this band increases considerably. Besides, another band of the stretching vibration of the bound C=O group was observed. The latter band may be assigned to the linear dimer. The low-frequency shifts of the bands of C=O stretching vibrations caused by the formation of intermolecular H-bonds in the cyclic dimers are 53 cm^{-1} for benzoic acid and 48 cm^{-1} for deuterobenzoic acid. The vibrations of the associates can be separated through comparison of the spectra obtained for samples with different matrix-to-sample ratios (Fig. 5c).

The data presented in Table 4 show that the AM1

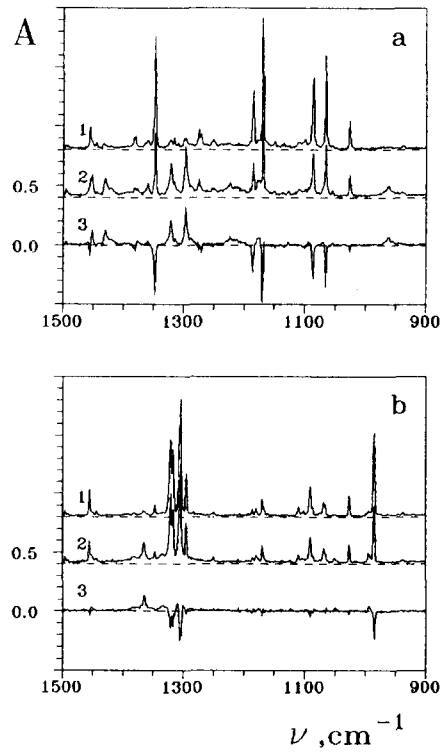

Fig. 6. C–O stretching and O–H (O–D) bending region. (a) Benzoic acid ($M/S = 250$). (b) Deuterobenzoic acid ($M/S = 750$). (1) Spectra after deposition at 17 K. (2) Spectra after matrix annealing at 30K for 30 min. (3) Difference spectra (3 = 2 − 1).

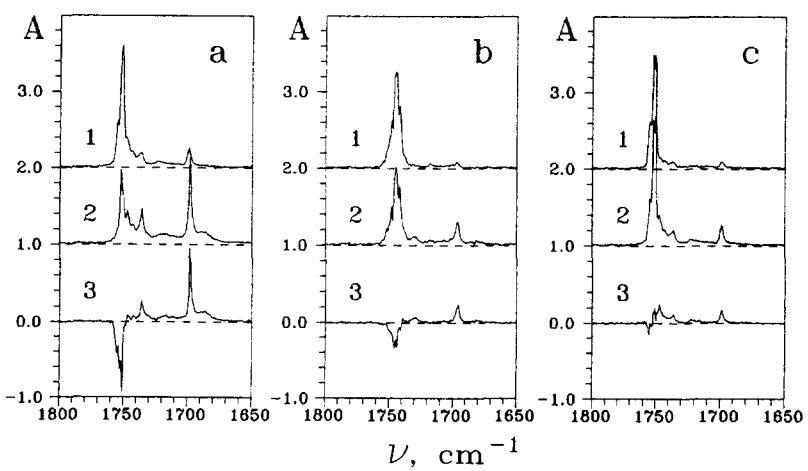

Fig. 5. C=O stretching region. (a) Benzoic acid ($M/S = 250$). (b) Deuterobenzoic acid ($M/S = 750$). For (a) and (b): (1) spectra after deposition at 17 K; (2) spectra after matrix annealing at 30 K for 30 min; (3) difference spectra (3 = 2 − 1). (c) Benzoic acid: (1) $M/S = 750$, spectrum after deposition at 17 K; (2) $M/S = 250$, spectrum after deposition at 17 K; (3) difference spectrum (3 = 2 − 1).

method underestimates the low-frequency shifts on the O–H (O–D) and C=O stretching vibrations. This is a consequence of the underestimation of intermolecular H-bond energies. Table 4 and Fig. 6 also present other frequencies of the benzoic acid dimers found from the analysis of the spectra obtained from the annealed samples and at different concentrations. These frequencies refer to the vibrations of the COOH group. Most bands assigned to the ring and C–H vibrations are evidently not affected by association.

5. Conclusions

The studies of the IR spectra of benzoic acid before and after annealing of the samples and at different concentrations show that IR spectroscopy in combination with the matrix-isolation method is an effective tool for identifying structural and spectral characteristics of monomers and associates of carboxyl containing compounds.

Along with monomers, the samples with $M/S = 750$ include cyclic symmetric dimers with two intermolecular H-bonds. The bands of the vibrations of these dimers are seen only in the spectra of annealed samples. The experimental IR spectra were analysed using normal coordinate analysis. The bands of dimers different from those of monomers were interpreted. It is shown that benzoic acid association affects only the frequencies of carboxyl vibrations. The ring and C–H vibrations are insensitive to association in dilute matrices.

As the molecule concentration in the matrix increases to $M/S = 250$, the bands of other associates appear in addition to the bands of monomers and cyclic dimers.

The potential energy surface of benzoic acid was calculated by the AM1 semiempirical method. It was found that the *syn* conformer is 5.5 kcal mol^{-1} more stable that the *anti* conformer. The frequencies of vibrations of the cyclic dimer show that the AM1 method underestimates the association-induced shifts in IR spectra as well the energies of intermolecular H-bonds in the benzoic acid dimers.

Acknowledgements

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